

# ARXPS analysis of a GaAs/GaInP heterointerface with application in III-V multijunction solar cells

M. Gabás , M.C. López-Escalante , C. Algora , I. Rey-Stolle , B. Galiana , S. Palanco , J.R. Ramos-Barrado

**Abstract** — In this contribution, angle-resolved X-ray photoelectron spectroscopy is used to explore the extension and nature of a GaAs/GaInP heterointerface. This bilayer structure constitutes a very common interface in a multilayered III-V solar cell. Our results show a wide indium penetration into the GaAs layer, while phosphorous diffusion is much less important. The physico-chemical nature of such interface and its depth could deleteriously impact the solar cell performance. Our results probe the formation of spurious phases which may profoundly affect the interface behavior.

**Index terms** — gallium arsenide, heterojunctions, III-V semiconductor materials, X-ray photoelectron spectroscopy, interface analysis.

## I. INTRODUCTION

Photoelectron spectroscopies (PES) are widely used in the surface and interface analysis. Usually, when incident photons are provided by X-ray sources they yield information on the first few nanometers of the layer. However the information depth can be easily modulated by varying the take-off angle of the emitted photoelectrons. Angle-resolved X-ray photoelectron spectroscopy (ARXPS) is thus a non-destructive analysis technique and moreover, the provided information is not affected by sample experimental damage, as it could happen when  $\text{Ar}^+$  sputtering is used in combination with PES, in order to study a buried surface or interface. An estimate of the sampling depth can be obtained taking into account that the photoelectrons mean free path is only dependent on both matrix effects and photoelectron kinetic energy. Thus, every core level will provide information up to a certain depth in the sample. ARXPS allows the selection of the mean information depth since data taken at small take-off angles supply information of the more superficial layers, while photoelectrons coming out at take-off angles close or equal to  $90^\circ$  provide information from a deeper level in the sample.

The interfaces between two layers of a III-V multijunction solar cell used in concentrator systems is a device critical part, since existing defects and impurities diffusion can profoundly affect the final device performance. III-V multijunction solar cells are made up of more than 20 different layers, with more than 6 different semiconductor elements, thicknesses varying from nanometer scale to 2 microns and with doping levels going from  $10^{17}$  to  $10^{20} \text{ cm}^{-3}$  [1]. Multijunction solar cells based on such complex structures have been able to achieve efficiencies well over 40% [2]. Every surface and interface in this layered structure is a potential object of analysis using PES techniques. One of the key tasks in these cells is the optimization of the heteroepitaxial growth of III-V layers onto the former one. A fundamental problem in III-V solar cells is the cross-diffusion during the epitaxial growth of different atoms at the various interfaces in the structure. The interfaces between two III-V semiconductors have received much attention because of their fundamental role on the performance of the solar cell device. In that way, the in-depth resolution that XPS can supply is of great relevance in order to determine the abruptness of a heterojunction. Their advantages as non-destructive and with a subnanometer in-depth resolution make ARXPS very competitive against secondary ion/neutral mass spectrometries (SIMS/SNMS) and the easy-handle sample management makes it more convenient than high resolution transmission electron microscopy (HRTEM).

A first approach to the GaAs/GaInP interface was done using X-ray photoelectron spectroscopy (XPS) in combination with  $\text{Ar}^+$  sputtering [3]. However, some of the effects on the sample surface due to the  $\text{Ar}^+$  sputtering process (preferred sputtering, metal reduction and Ar implantation) were detected in our study. In order to avoid such undesirable effects, an ARXPS analysis has been conducted and it is presented in this contribution.

## II. EXPERIMENTAL

A multilayer III-V semiconductor structure was grown by MOVPE (Metal Organic Vapour Phase Epitaxy). It is made up of an undoped GaAs cap layer, a tellurium doped GaInP and a final undoped GaAs layer on a SI-GaAs substrate. The nominal layer thicknesses were 5, 338 and 407 nanometers, respectively. This structure contains a GaAs/GaInP heterointerface which is common in III-V multijunction solar cells.

ARXPS spectra were recorded on a Physical Electronics PHI 5700 spectrometer using non-monochromated Mg  $K\alpha$  and Al  $K\alpha$  radiation ( $h\nu = 1253.6$  and  $1486.6$  eV, respectively). The acceptance angle of the analyzer has been set to  $14^\circ$  and the angle between the incident X-rays and the analyzer is  $54^\circ$ . The direction of the outgoing photoelectrons is given by the polar angle  $\theta$ , referred to the sample surface and the azimuth. In order to obtain angle dependent XPS results, the polar angle is varied from  $30^\circ$  to  $90^\circ$ . The different take-off angles were used to vary the photoelectron path in the solid and hence the sampling depth, with the smaller take-off angle being more surface sensitive. The core level spectra were fitted using the XPSPeak software package [4].

## III. RESULTS

Photoelectrons leaving the sample surface have a different escape length depending on their kinetic energy. The corresponding inelastic mean free path (IMFP) multiplied by  $\sin\theta$  allows to estimate this escape length. Every core level is thus a probe from a different depth under the sample surface.

Core levels  $2p_{3/2}$  from both, Ga and As elements have the smaller escape depth since the photoelectron kinetic energies coming out the surface layer are very low. In figure 1, the obtained XPS signal from Ga  $2p_{3/2}$  (top) and As  $2p_{3/2}$  (bottom) at various take-off angles are depicted. For these two core levels the escape depths run from  $\sim 0.65$  to  $\sim 1.35$  nm, corresponding to polar angles  $30^\circ$  and  $90^\circ$ , respectively. As it is shown in figure 1, As  $2p_{3/2}$  shape evolves as the escape depth does, while Ga  $2p_{3/2}$  maintains a very similar profile.

A detailed analysis of these signals indicates that Ga is more oxidized than As at the surface layer which is in accordance with some other previous reports [5]. The deconvolution of Ga  $2p_{3/2}$  and As  $2p_{3/2}$  core level signals measured with a take-off angle of  $30^\circ$  are depicted in Figure 2 with their corresponding fits. The mean escape depth corresponding to these analyses is 0.65 nm. Oxidized Ga is in the form  $Ga_2O_3$  while As presents two oxidation states,  $As_2O_3$  and  $As_2O_5$ . The binding energy shifts among the various constituents in the As  $2p_{3/2}$

signal are in good agreement with those presented in previous literature [6].

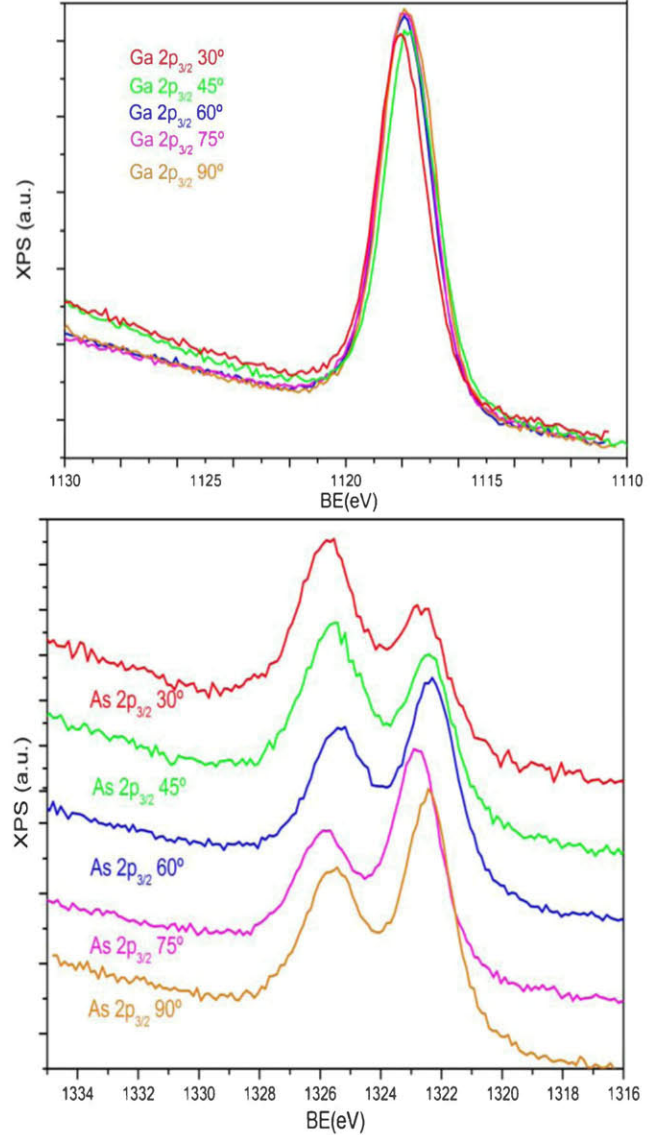


Fig. 1: Ga  $2p_{3/2}$  (top) and As  $2p_{3/2}$  (bottom) core levels XPS signal at various take-off angles.

To investigate the diffusion of elements from the buried GaInP layer into the GaAs cap layer, the P 2p and the In 3d core levels have been monitored at the different take-off angles. P 2p core level is not detectable up to 3.5 nm deep in the GaAs layer. Assuming the nominal thickness of 5 nm for the GaAs cap layer, phosphorus diffusion is limited to a small length across the interface.

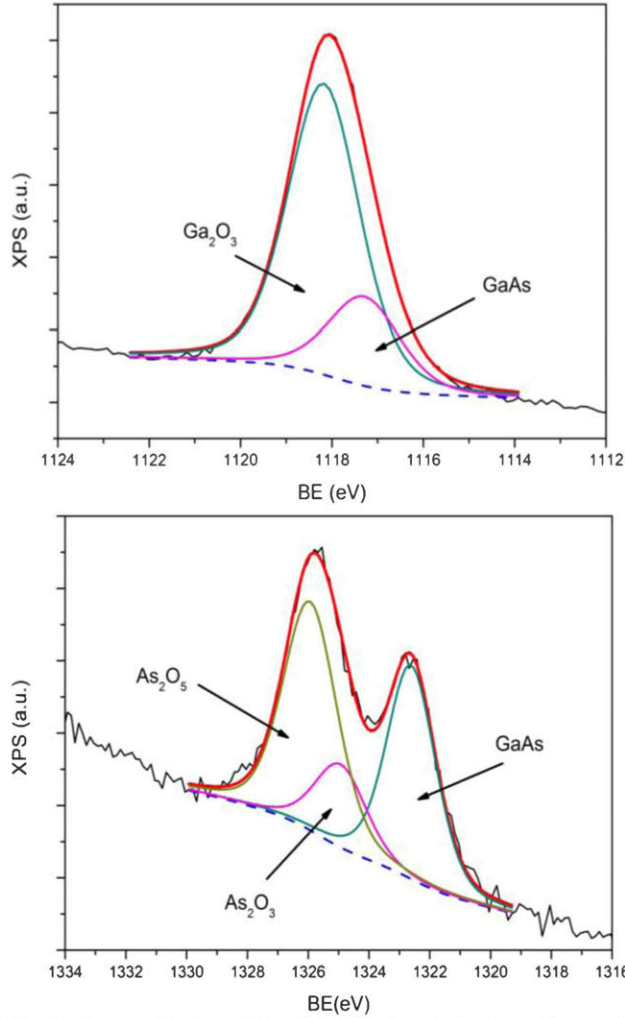


Fig. 2: deconvolution of Ga  $2p_{3/2}$  (top) and As  $2p_{3/2}$  (bottom) core levels XPS signals. The different constituents are labeled in the figures.

On the contrary, In 3d core level is measurable at the surface of the GaAs layer. The penetration of this element reaches the whole thickness of the GaAs cap layer. The analysis of the In 3d core level at  $30^\circ$  and  $90^\circ$  take-off angles shows that this element is partially oxidized, although the  $\text{In}_2\text{O}_3$  quantity decreases quickly as the sampling depth does, which implies a thin In oxide layer at the film surface. In figure 3, the deconvolution of the In3d core level signal at two different take-off angles,  $30^\circ$  (top) and  $90^\circ$  (bottom), is presented. The spin orbit splitting (SOS) factor is 7.54 eV. For the two escape lengths –1.5 nm ( $30^\circ$ ) and 3.1 nm ( $90^\circ$ )– there are two contributions in the PE spectra. The one at higher binding energies represents the 30% of the global intensity for the data taken at  $30^\circ$ , while it diminishes to 15% when data are collected at  $90^\circ$ . That points to the presence of  $\text{In}_2\text{O}_3$  as a thin layer at the topmost layer surface. The main

contribution is probably due to the formation of an InAs phase or an InGaAs phase. They would be undistinguishable since the In3d core level binding energy should be very similar given that they both have the same crystallographic structure. The presence of the ternary phase GaInP should be discarded at this point, since the P 2p signal is negligible up to 3.5 nm deep in the layer. The signal-to-background ratio increases as the escape depth do, suggesting thus an enrichment of the In content in the layer when approaching the GaAs/GaInP interface.

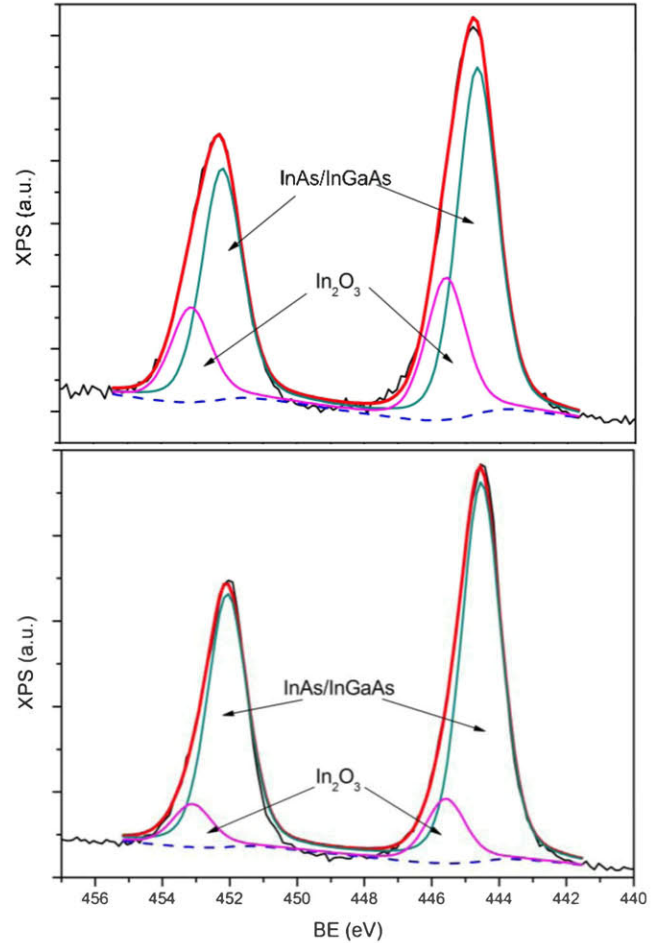


Fig. 3: deconvolution of the In 3d core level signal, data taken at take-off angles  $30^\circ$  (top) and  $90^\circ$  (bottom) which correspond to escape depths of 1.5 and 3.1 nm, respectively.

On the other hand, 3d core levels from Ga and As give information up to 1.9 nm ( $30^\circ$ ) or 3.8 nm ( $90^\circ$ ) deep under the film surface. Figure 4 shows the deconvolution of the 3d core level signal taken at  $30^\circ$ , for both, As (top) and Ga (bottom). The different constituents are doublets with SOS values of 0.69 eV (As 3d) and 0.44 eV (Ga 3d). The As 3d signal has two contributions, which can be ascribed to  $\text{As}_2\text{O}_3$  (BE = 44.4 eV) and a mixture of both arsenides



GaAs and InAs or a InGaAs phase with an In content increasing with depth, according to what has been found in the analysis of In3d core level. The estimated escape depth at 30° for photoelectrons coming from these core levels are 1.5 nm and 1.9 nm, for In3d and As3d respectively. According to that, the information from these core levels is complementary. Ga 3d core level has a rather complicated spectrum since the In 4d core level (SOS = 0.86 eV) is in the same energy region (~17eV). Thus, it should be included in the signal deconvolution (see figure 4 bottom). In that way, Ga3d core level has 4 contributions, the one at bigger binding energies corresponds to the oxide Ga<sub>2</sub>O<sub>3</sub>, the main one being the GaAs. The ones at lower binding energies correspond to the In4d core level from the InAs or InGaAs phase and the In<sub>2</sub>O<sub>3</sub>.

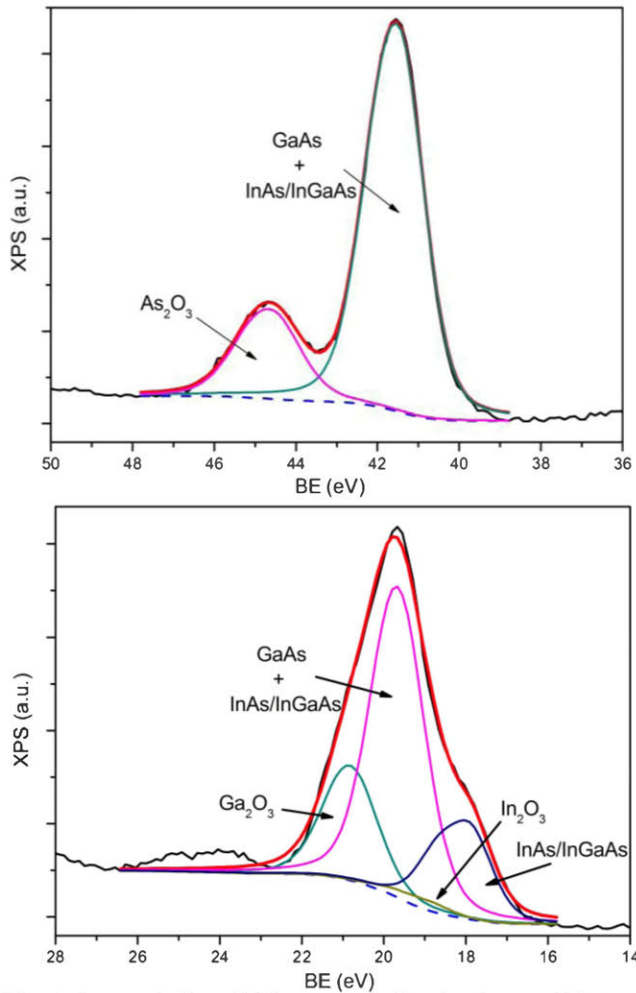


Fig. 4: deconvolution of 3d core level signals taken at 30°: As (top) and Ga (bottom).

The data obtained from these core levels measured at 60° polar angle (mean escape depth ~3.3 nm) looked very

similar to those taken at 30°, and the deconvolution analysis (not shown here) varied only in the diminishing quantity of oxides contribution intensities. However, the data measured at 90° (mean escape depth ~3.8 nm) show an important difference compared to the former ones. The main signal component diminishes its full width at half maximum: from 1.35 to 1.1 eV for the As 3d core level and from 1.4 to 1.1 eV for the Ga 3d core level (see figure 5). The intensity of the contribution from oxides in both core levels has diminished, being negligible for the In<sub>2</sub>O<sub>3</sub>.

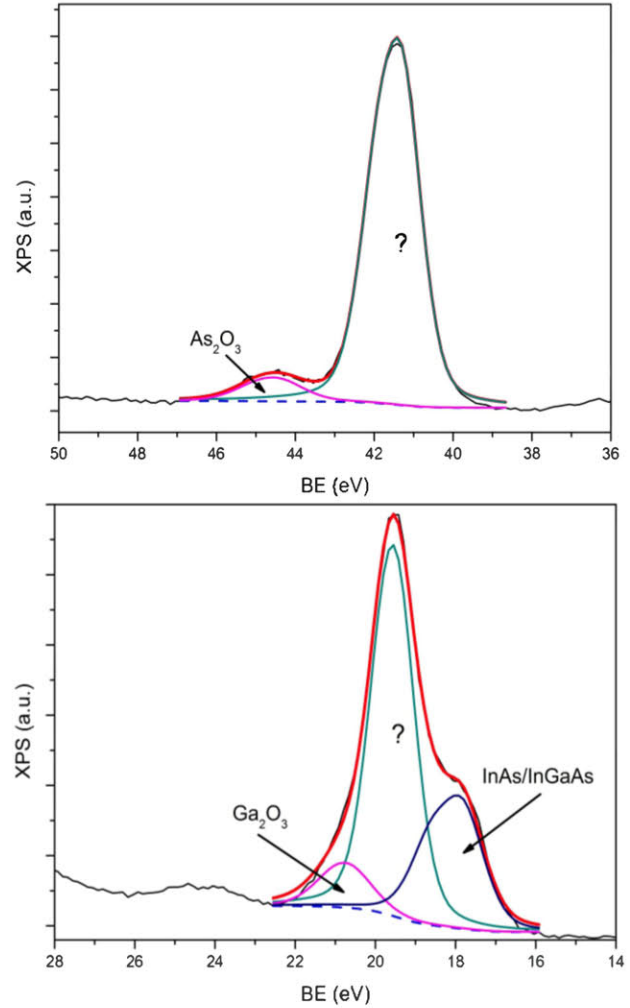


Fig. 5: deconvolution of 3d core level signals taken at 90°: As (top) and Ga (bottom).

This fact is maybe related with the above mentioned In enrichment when approaching the interface and/or with the formation of new phases due to the presence of P at depths bigger than 3.5 nm. The composition of these phases Ga would be uncertain. In that way, the quantity of pure GaAs phase would have diminished significantly close to the interface or it would be distorted.

#### IV. SUMMARY AND CONCLUSIONS

ARXPS has been used in the study of a GaAs/GaInP heteroface which is very common in III-V multijunction solar cells. In spite of such interface was grown by MOVPE and was intended to be abrupt, the ARXPS measurements show an In penetration into the cap GaAs layer. The formation of spurious phase like InAs or more probably an InGaAs intermediate compound is strongly suggested. Our experimental data evidences an In enrichment close to the “nominal” GaAs/GaInP interface, which would support the formation of the InGaAs phase. The formation of new spurious phases with unknown composition and/or the GaAs phase distortion cannot be discarded. Therefore, ARXPS seems to be of great help in the study and experimental optimization of heterofaces of III-V multijunction solar cells.

#### ACKNOWLEDGMENTS

This work has been supported by the Spanish Ministerio de Economía y Competitividad with the projects TEC2011-28639-C02-01 and -02 and with the INNPACTO program by means of the IPT-2011-1441-920000 and IPT-2011-1408-420000 projects. This project has been also supported by the Comunidad de Madrid under the NUMANCIA II program (S2009/ENE1477).

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